

## SPECIFICATION

## NONAQUEOUS SECONDARY BATTERY WITH LITHIUM TITANIUM CATHODE

## FIELD OF THE INVENTION

5 This application is the national phase under 35 U.S.C.  
\$371 of prior PCT International Application No.  
PCT/JP97/02008 which has an International filing date of  
June 11, 1997 which designated the United States of America,  
the entire contents of which are hereby incorporated by  
10 reference.

The present invention relates to a lithium secondary  
cell. In particular, the present invention pertains to  
lithium secondary cells suitable as backup batteries for  
watches, power sources for portable devices such as pagers,  
15 timers, etc., backup batteries for memories, and the like.

## PRIOR ART

Lithium secondary cells comprising a negative electrode  
made of metal lithium or a lithium alloy have been mainly  
developed as secondary cells. However, when the metal  
20 lithium or lithium alloy is contained in the negative  
electrode, lithium ions in an electrolyte tend to  
precipitate in the form of metal lithium on the negative  
electrode during recharging. The deposited lithium forms  
minute particles or grows lithium dendrites on the surface  
25 of the negative electrode, and causes a short-circuit in the  
cell. Thus, the charge-discharge cycle life of the cell is  
shortened. Consequently, lithium cells, which use neither

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metal lithium nor a lithium alloy in the negative electrode and have a high energy density, have been studied.

Currently, primary cells such as silver oxide cells are used as power sources for wristwatches. However, the primary cells suffer from problems associated with disposal of the used cells. Thus, wristwatches having built-in power generators, which require no replacement of the cells, have been developed, and electric double layer capacitors are used as power sources used in such wristwatches. However, the electric double layer capacitors have a small capacity per unit volume, and thus it is desired to develop substitute power sources for the electric double layer capacitor.

#### SUMMARY OF THE INVENTION

One object of the present invention is to provide a lithium secondary cell which can be charged and discharged, does not suffer from the problem of disposal, and has a high capacity so that it is suitable as a power source for a wristwatch.

Accordingly, the present invention provides a lithium secondary cell comprising a positive electrode containing lithium titanate as an active material, a negative electrode containing a carbonaceous material as an active material, and an electrolytic solution comprising a solution of a lithium salt in an organic solvent.

Since a lithium titanate as a positive electrode active material and a carbonaceous material as a negative electrode

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active material are used in combination, the lithium ions can be easily doped and dedoped at a nominal voltage of 1.5 V, and thus a lithium secondary cell having a high capacity and good charge-discharge cycle properties is obtained.

## 5 BRIEF DESCRIPTION OF THE INVENTION

Fig. 1 is a cross section of an example of a lithium secondary cell according to the present invention.

Fig. 2 is a graph showing the discharge properties of the cells of Examples 1 and 2 and comparative Example 1 in the first discharge.

Fig. 3 is a graph showing the charge-discharge cycle properties of the cells of Examples 1 and 2 and comparative Example 1.

## DETAILED DESCRIPTION OF THE INVENTION

15 A lithium titanate used as a positive electrode active material according to the present invention can be prepared by heating titanium oxide and a lithium compound at a temperature of between 760 and 1100°C.

In general, the lithium titanate is represented by the formula (1):



Usually, x and y in the above formula are numerals in the range between 0.8 and 1.4 ( $0.8 \leq x \leq 1.4$ ), and between 1.6 and 2.2 ( $1.6 \leq y \leq 2.2$ ), respectively. In particular, the lithium titanate of the formula (1) in which x is 1.33 and y is 1.67 is preferable.

Titanium oxide may be either anatase or rutile. The lithium compound may be lithium hydroxide, lithium carbonate, lithium oxide, and the like.

A positive electrode is preferably prepared by mixing lithium titanate, a conducting aid and a binder to obtain a positive electrode mixture, and shaping the mixture under pressure.

Examples of the conducting aid are scaly graphite, acetylene black, carbon black, and the like. Fluororesins are preferably used as binders. Examples of fluororesins are polytetrafluoroethylene, polyvinylidene fluoride, and the like.

Proportions of the components constituting the positive electrode are preferably 70 to 90 wt. % of the lithium titanate as the positive electrode active material, 5 to 20 wt. % of the conducting aid, and 1 to 10 wt. % of the binder.

When the amount of the lithium titanate is less than the above lower limit, the capacity of the cell tends to decrease and high capacity may not be achieved. When the amount of the lithium titanate exceeds the above upper limit, the amounts of the electrical conducting aid and binder decrease correspondingly, and the conductivity or strength of the positive electrode mixture may decrease.

When the amount of the conducting aid is less than the above lower limit, the electrical conductivity may decrease. When the amount of the conducting aid exceeds the above

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upper limit, the amount of the lithium titanate decreases correspondingly and the capacity of the cell may decrease.

When the amount of the binder is less than the above lower limit, the integrity of the positive electrode mixture may decrease and shaping of the mixture may become difficult. When the amount of the binder exceeds the above upper limit, the amount of the lithium titanate decreases correspondingly and the capacity of the cell may decrease.

The production method for the positive electrode is not limited to the above method, and compositions of the components are not limited to the above described one.

A negative electrode is preferably prepared by mixing a carbonaceous material as a negative electrode active material and a binder to obtain a negative electrode mixture, and shaping the mixture under pressure.

Examples of the carbonaceous material as the negative electrode active material are synthetic graphite, natural graphite, low crystalline carbon, coke, anthracite (hard coal), and the like. In particular, synthetic graphite is preferable, since it can achieve the higher capacity than other carbonaceous materials.

Fluororesins are preferably used as binders. Examples of fluororesins are polytetrafluoroethylene, polyvinylidene fluoride, and the like.

The proportions of the components constituting the negative electrode are preferably 80 to 95 wt. % of the

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carbonaceous material as the negative electrode active material and 5 to 20 wt. % of the binder.

When the amount of the carbonaceous material as the negative electrode active material is less than the above lower limit, it may be difficult to obtain a lithium secondary cell having a high capacity. When the amount of the carbonaceous material exceeds the above upper limit, the amount of the binder decreases, and thus the integrity of the positive electrode mixture may decrease and shaping of the mixture may become difficult.

The production method for the negative electrode is not limited to the above method, and compositions of the components are not limited to the above described one. For example, a conducting aid may be added to the negative electrode mixture.

In the present invention, the cell comprises an electrolytic solution which is prepared by dissolving a lithium salt in an organic solvent. Examples of the organic solvent used as the solvent for the electrolytic solution are propylene carbonate, ethylene carbonate, butylene carbonate,  $\gamma$ -butyrolactone, 1,2-dimethoxyethane, dimethoxymethane, tetrahydrofuran, dioxolane, and the like.

Examples of the lithium salt are  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ,  $\text{LiClO}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiSbF}_6$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiCF}_3\text{CO}_2$ ,  $\text{LiC}_n\text{F}_{2n+1}\text{SO}_3$  ( $n \geq 2$ ),  $\text{LiN}(\text{CF}_3\text{CF}_2\text{SO}_2)_2$ , and the like. Among them,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ,  $\text{LiPF}_6$ ,  $\text{LiCF}_3\text{SO}_3$  and  $\text{LiBF}_4$  are preferably used since they have high conductivity, and are thermally stable.

The concentration of the lithium salt in the electrolytic solution is not limited, and is usually between 0.1 and 2 mole/l, preferably between 0.4 and 1.4 mole/l.

The structure and production method of the lithium secondary cell of the present invention are substantially the same as those of conventional lithium secondary cells except that the above positive and negative electrodes and electrolytic solution are used.

#### EXAMPLES

The present invention will be illustrated by the following Examples, which do not limit the scope of the present invention in any way.

##### Example 1

Anatase titanium oxide (2 moles) and lithium hydroxide (1 mole) were mixed and calcined using an electric furnace in air at 800°C for 8 hours, and a lithium titanate was obtained. The composition of this lithium titanate was analyzed by atomic absorption analysis, and found to be  $\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$ .

The obtained lithium titanate (100 wt. parts), carbon black (5 wt. parts) and graphite (5 wt. parts) as conducting aids, and polytetrafluoroethylene (5 wt. parts) as a binder were mixed in isopropanol to prepare a positive electrode mixture. After evaporating off the solvent, the positive electrode mixture was molded in the form of a pellet having a diameter of 6.0 mm and a thickness of 0.5 mm. The pellet

was dried and dehydrated with a far-infrared drier at 250°C for 30 minutes to form a positive electrode.

Separately, synthetic graphite (90 wt. parts) and polyvinylidene fluoride (10 wt. parts) as a binder were mixed in N-methylpyrrolidone to prepare a negative electrode mixture. After evaporating off the solvent, the negative electrode mixture was molded in the form of a pellet having a diameter of 3.5 mm and a thickness of 1.0 mm. The pellet was dried and dehydrated with a far-infrared drier at 120°C for 30 minutes to form a negative electrode.

An electrolytic solution, which was prepared by dissolving  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  in a mixed solvent of ethylene carbonate and diethyl carbonate in a volume ratio of 1:1 at a concentration of 1.0 mole/l, was used.

Using the above positive and negative electrodes and electrolytic solution, a lithium secondary cell having the structure shown in Fig. 1 and an outer diameter of 6.7 mm and a height of 2.1 mm was assembled.

In Fig. 1, a positive electrode 1 consisted of a press molded article of a positive electrode mixture containing the lithium titanate ( $\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$ ) as an active material, carbon black and graphite as conducting aids, and polytetrafluoroethylene as a binder.

A negative electrode 2 consisted of a press molded article of a negative electrode mixture containing synthetic graphite as an active material and polyvinylidene fluoride as a binder.

A separator 3 made of polypropylene non-woven fabric was inserted between the positive electrode 1 and negative electrode 2.

During assembling of the cell, the negative electrode 2 was doped with lithium ions in the presence of an electrolytic solution while placing metal lithium in an amount corresponding to 80 % of the electric capacity of the positive electrode on the opposite side of the separator 3.

The positive electrode 1, negative electrode 2, separator 3 and electrolytic solution were sealed in a space formed by a positive electrode can 4 made of stainless steel, a negative electrode can 5 made of stainless steel, and an insulation packing 6 made of polypropylene.

#### Example 2

A lithium secondary cell was produced in the same manner as in Example 1 except that an electrolytic solution, which had been prepared by dissolving  $\text{LiPF}_6$  in place of  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  in a mixed solvent of ethylene carbonate and diethyl carbonate in a volume ratio of 1:1 at a concentration of 1.0 mole/l, was used.

#### Comparative Example 1

A lithium secondary cell was produced in the same manner as in Example 1 except that lithium iron oxide ( $\text{LiFe}_2\text{O}_4$ ) was used as a positive electrode active material in place of a lithium titanate.

Each of the cells produced in Examples 1 and 2 and Comparative Example 1 was charged and discharged under the

following conditions, and the discharge property in the first discharge, and the charge-discharge cycle property were evaluated:

Charging conditions: constant current, 0.1 mA and  
charge cut voltage, 2.4 mA  
Discharging conditions: constant current, 0.1 mA and  
discharge cut voltage, 0.4 mA

The discharge properties in the first discharge are shown in Fig. 2, and the charge-discharge properties are shown in Fig. 3.

As seen from Fig. 2, the cells of Examples 1 and 2 had better flatness of the cell voltage around 1.5 V and larger cell capacity down to 0.4 V than the cell of Comparative Example 1. Thus, the cells of Examples 1 and 2 had a high capacity.

As seen from Fig. 3, the cells of Examples 1 and 2 had the larger cell capacity than the cell of Comparative Example 1 after the same number of cycles. Furthermore, the former cells suffered less decrease of cell capacity due to the increase of the number of cycles than the latter cell. That is, the cells of Examples 1 and 2 had good charge-discharge cycle properties.

In contrast, the cell of Comparative Example 1 had a small cell capacity, and the cell capacity dropped sharply in the early cycles of charge and discharge. That is, this cell had low charge-discharge cycle properties. These properties of the cell of Comparative Example 1 may be

attributed to the destabilization of the crystal structure of lithium iron oxide, which was used as the positive electrode active material, during the charge and charge cycles.

A lithium secondary cell was produced in the same manner as in Example 1 or 2 using the same electrolytic solution and negative electrode, and the lithium titanate having the composition of  $\text{Li}_7\text{Ti}_2\text{O}_4$  or  $\text{Li}_{0.8}\text{Ti}_{2.2}\text{O}_4$  in place of  $\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$ , and a cell capacity and charge-discharge cycle properties were evaluated. The results were the same as those in Examples 1 and 2.

As explained above, the present invention can provide lithium secondary cells having a high capacity and good charge-discharge cycle properties at a nominal voltage of 1.5 V, since a lithium titanate of the formula:  $\text{Li}_x\text{Ti}_y\text{O}_4$  is used as a positive electrode active material, and a carbonaceous material such as synthetic graphite is used as a negative electrode active material.